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CCL REPORT NO. 251

FINAL REPORT

STORAGE OF ETHYLENE GLYCOL ANTIFREEZE IN UNLINED TIN CONTAINERS

BY

JAMES H. CONLEY

JULY 1968

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FINAL REPORT

STORAGE OF ETHYLENE GLYCOL ANTIFREEZE IN UNLINED TIN CONTAINERS

BY

JAMES H. CONLEY

JULY 1968

AMCMS CODE NO. 5025.11.80300

DEPARTMENT OF THE ARMY PROJECT NO.
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U. S. ARMY COATING AND CHEMICAL LABORATORY
ABERDEEN PROVING GROUND
MARYLAND

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ABSTRACT

The object of this study was to investigate the effect of pH on the package stability of mercaptobenzothiozole-borax inhibited ethylene glycol antifreeze compounds. The antifreeze compounds were packaged in unlined tin plated containers for a two-year period.

Results show that antifreeze compounds with pH values below 10.3 caused corrosion in less than six months. Containers filled with compounds having pH values above 10.3 showed some corrosion in one year and were generally unsatisfactory after two years storage. Most of the attack was at the junction of the bottom and side seams of the containers.

TABLE OF CONTENTS

I. INTRODUCTION

Aberdeen Proving Ground, Maryland, was directed by AMC program directive AMCMS Code No. 5025.11.80300 dated 22 September 1967 to investigate improved antifreeze compounds.

A large number of commercial antifreeze compounds in use today contain combinations of borate type inhibitors and mercaptobenzothiazole (MBT) or alkali metal salts of mercaptobenzothiazole. These compounds are usually packaged in tin containers, some of which have organic liners. They contain less than 0.05% MBT and are packaged at pH values of about 9.5. This is less than the desired amount of MBT needed for good service performance.

Corrosion difficulties have been encountered in the packaging of ethylene glycol antifreezes, especially if large amounts of MBT are present in the inhibitor system. MBT caused some corrosion in tin plated containers around the soldered side seam and considerably more at the point of junction of the side and bottom seams.

Undiluted ethylene glycol containing borax as an inhibitor composes Federal Specification O-A-548, Type I, antifreeze. This material is specified for Army use by TB-ORD-651. It has an acidic pH (below 7.0) and tends to cause corrosion of tin containers in storage. Chemically, MBT is an acid. However, in diluted glycol mixtures in which the pH is buffered above 7.0, the presence of MBT greatly enhances the inhibitive properties of borax. Therefore, it is one of the constituents of Federal Specification O-I-490a, Inhibitor, Corrosion, Liquid Cooling System. This material is used in conjunction with O-A-548, Type I, antifreeze and is specified for Army use by TB-ORD-651.

Preliminary data in CCL Reports No. 86 and No. 100 showed that tin panels immersed in undiluted ethylene glycol containing borax and 0.25% MBT were unsatisfactory after 8 months storage. Test solution pH values were below 7.0. Tin panels in solutions with pH values of 10.5 and containing 3% water were satisfactory after 8 months storage. Data also showed that tin panels in solutions containing 0.5% NACAP and 3% water were unsatisfactory both at low pH values and at pH values up to 10.5.

The present study was initiated to determine if an antifreeze compound containing enough MBT to give satisfactory service performance could be stored in unlined tin plated containers for a two year period by increasing the packaged pH value.

IV. DISCUSSION AND CONCLUSIONS

The data clearly shows that antifreeze compounds containing mercaptobenzothiazole packaged in unlined tin plated containers at pH values below 10.3 caused corrosion in six months. Antifreeze compounds with pH values above 10.3 caused corrosion at the junction of the side and bottom seams in two years.

Data in CCL Report No. 210 showed that antifreeze compounds having pH values above 8.5 are deleterious to both solder and aluminum radiator components during vehicle operation. If these metals are used, the most desirable pH values are in the range of from 7.5 to 8.2. Therefore, the problem of packaging antifreeze compounds becomes a function of the pH versus the type of container. The military have overcome this problem by specifying separate containers for the coolant and the inhibitor combination. This is not the most desirable solution from the logistics standpoint and causes some confusion in the field. It would be much better if a single package could be used.

V. RECOMMENDATIONS

It is recommended that a study of the storage of antifreeze in polyolefin containers be conducted. This will eliminate metal attack, will eliminate dual packaging of the coolant and inhibitor, simplify procurement and assure the use of the specified amount of inhibitor in the field. At the present time commercial antifreeze suppliers are in the process of switching to polyolefin containers.

VI. REFERENCES

1. Authority - AMC program directive AMCMS Code No. 5025.11.80300 dated 22 September 1967.

2. TB-ORD-651, Use of Antifreeze Solutions in Engine Cooling Systems, dated 10 April 1964.

3. Federal Specification O-A-548a, Antifreeze, Ethylene Glycol, Inhibited, Type I, dated 30 December 1958.

4. Federal Specification O-I-490a, Inhibitor, Corrosion, Liquid Cooling System, dated 26 April 1965.

5. Federal Specification PPP-C-96, Cans, Metal, 28 Gage and Lighter, dated 29 March 1955.

6. CCL Report No. 86, Study of a Newly Developed Inhibitor for Ethylene Glycol in Storage, dated December 1959.

7. CCL Report No. 100, Storage of Ethylene Glycol With Various Inhibitors, dated March 1961.

8. CCL Report No. 210, Effect of Coolants on Various Types of Aluminum Alloys, dated October 1966.

APPENDIX A

TABLE I

Composition of Test Solutions - Percent by Weight

	Series A				
	1	2	3	4	5
Ethylene Glycol	90.85	90.85	90.85	90.85	90.85
Distilled Water	4.85	4.85	4.85	4.85	4.85
Borax	4.00	4.00	4.00	4.00	4.00
Sodium Mercaptobenzothiazole (NACAP)	0.30	0.30	0.30	0.30	0.30
Added Sodium Hydroxide	0.84	0.85	0.86	0.87	0.90

	Series B				
	1	2	3	4	5
Ethylene Glycol	90.90	90.90	90.90	90.90	90.90
Distilled Water	4.90	4.90	4.90	4.90	4.90
Borax	4.00	4.00	4.00	4.00	4.00
Sodium Mercaptobenzothiazole (NACAP)	0.20	0.20	0.20	0.20	0.20
Added Sodium Hydroxide	0.84	0.85	0.86	0.87	0.90

	Series C				
	1	2	3	4	5
Ethylene Glycol	90.95	90.95	90.95	90.95	90.95
Distilled Water	4.95	4.95	4.95	4.95	4.95
Borax	4.00	4.00	4.00	4.00	4.00
Sodium Mercaptobenzothiazole (NACAP)	0.10	0.10	0.10	0.10	0.10
Added Sodium Hydroxide	0.84	0.85	0.86	0.87	0.90

TABLE II

Initial pH Values of Test Solutions

	Pkg pH	50% pH	30% pH
1 - A	8.30	9.50	9.85
2 - A	8.58	9.62	9.85
3 - A	8.80	9.82	10.05
4 - A	10.32	10.42	10.49
5 - A	10.80	11.02	11.08
1 - B	8.23	9.47	9.82
2 - B	8.38	9.62	9.93
3 - B	8.55	9.75	10.02
4 - B	8.88	9.93	10.20
5 - B	10.65	10.82	10.85
1 - C	8.12	9.42	9.72
2 - C	8.25	9.50	9.85
3 - C	8.55	9.75	10.05
4 - C	9.30	10.13	10.32
5 - C	10.65	10.85	10.89

TABLE III

Inspection of Containers After Six Months Storage

	pH	Can Appearance Filled	Can Appearance Empty
1 - A	8.50	Black over most surfaces	Surface dark and pitted
2 - A	8.65	Mod. sediment at seam joint	V. sl. pitting at seam joints
3 - A	8.88	Sl. - Mod. sediment at seam joint	V. sl. pitting at seam joint
4 - A	10.08	V. sl. sediment	V. sl. pitting at seam joint
5 - A	11.52	O.K.	O.K.
1 - B	8.30	Rusty sed. at bottom joint	V. sl. pitting at seam joint
2 - B	8.42	Rusty sed. at bottom joint	Sl. pitting at seam joint
3 - B	8.58	V. sl. sed. at bottom joint	V. sl. pitting at seam joint
4 - B	8.92	Sl. sed. at bottom joint	V. sl. pitting at seam joint
5 - B	11.12	V. sl. rusting at bottom joint	V. sl. pitting at seam joint
1 - C	8.15	V. sl. sed. at bottom joint	V. sl. pitting at seam joint
2 - C	8.32	V. sl. sed. at bottom joint	V. sl. pitting at seam joint
3 - C	8.55	V. sl. sed. at bottom joint	V. sl. pitting at seam joint
4 - C	9.02	Mod. sed. at bottom joint	Mod. pitting at seam joint
5 - C	11.08	O.K.	O.K.

TABLE IV

Inspection of Containers After One Year's Storage

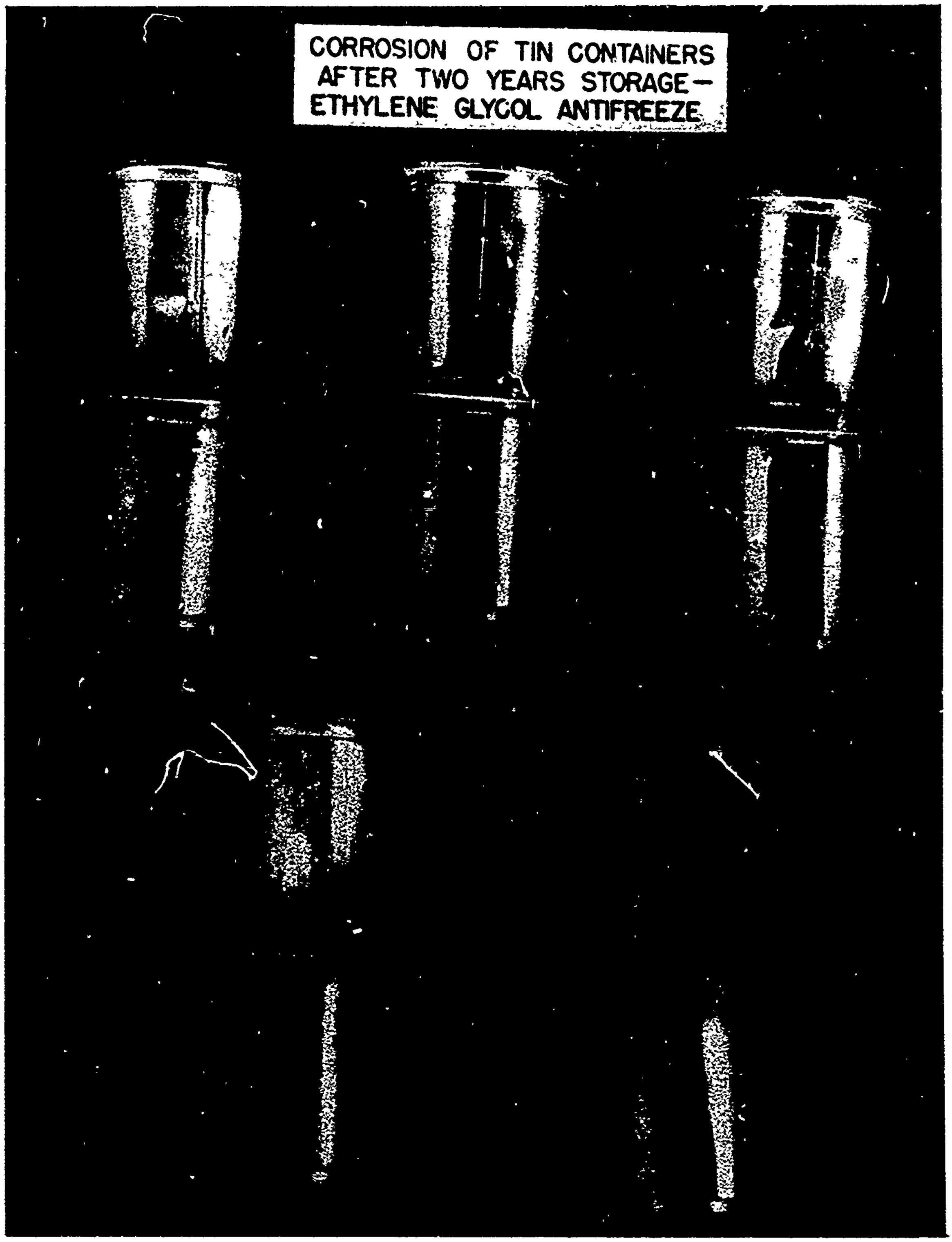
	pH	Can Appearance Filled	Can Appearance Empty
1 - A	8.58	Black over entire surface	Surface dark & pitted, heavy corr. on seam
2 - A	8.72	Heavy sed. at seam joint, vapor phase corrosion	Sl. pitting at seam joint
3 - A	8.99	Mod. - Heavy sed., vapor phase corrosion	Sl. pitting at seam joint, 2 heavy spots
4 - A	10.53	Light sed. at seam joint	Sl. pitting at seam joint
5 - A	11.49	O.K.	V. sl. pitting on side seam near bottom
1 - B	8.25	Rusty sed. at seam joint, vapor phase corrosion	Sl. pitting at seam joint
2 - B	8.42	Rusty sed. at seam joint	Pitted over 1/2 bottom seam, spots on seam side
3 - B	8.52	Light sed. at seam joint, vapor phase corrosion	Sl. pitting at seam joint, scattered spots
4 - B	8.82	Mod. sed. at seam joint	Sl. pitting at seam joint & all over side seam
5 - B	11.20	O.K.	V. sl. pitting at seam joint
1 - C	8.18	Light rusty sed. at seam joint	Sl. pitting at seam joint, spots on side seam
2 - C	8.30	Light rusty sed. at seam joint, vapor phase corrosion	Sl. pitting at seam joint, spots on side seam
3 - C	8.60	Light rusty sed. at seam joint	Sl. pitting at seam joint, spots on side seam
4 - C	8.87	Heavy rusty sed.	Pitting over 1/2 of bottom seam & side seam
5 - C	11.22	O.K.	Sl. pitting at seam joint, spots on side seam

TABLE V

Inspection of Containers After Two Year's Storage

	pH	Can Appearance Filled	Can Appearance Empty
1-A	8.35	Mod. sed. mod-heavy pitting on side and bottom joint	Mod.-heavy pitting on side, sl. pitting at bottom joint
2-A	8.68	Mod. sed. at joint, pitting on side seam and along bottom seam with scattered spots	Scattered spot corrosion, sl.-mod. pitting at bottom seam joint
3-A	8.78	Mod. sed. at joint, corrosion all along side seam, vapor phase corrosion	Scattered spot corrosion, sl.-mod. pitting on side seam, sl. pitting at bottom joint
4-A	10.50	V. sl. sed. pitting on side seam	Sl. pitting on side seam and bottom joint
5-A	11.43	Soln. clear, spot corrosion & pitting on side seam, vapor phase corrosion	Mod.-heavy pitting on side seam, v. sl. pitting at bottom joint
1-B	8.22	Mod. sed., sl. pitting on side seam	Sl. pitting on side seam & bottom joint
2-B	8.37	Mod. sed., sl.-mod. pitting on side & bottom seam, vapor phase corrosion	Sl.-mod. pitting on side seam, sl. pitting at bottom joint
3-B	8.52	Mod. sed., sl. pitting on side seam	Sl. pitting on side seam, sl.-mod. pitting at bottom joint
4-B	8.93	Mod. sed., sl.-mod. pitting on side seam, vapor phase corrosion	Sl. pitting on side seam and bottom joint
5-B	11.10	Soln. clear, sl. pitting on side seam and bottom joint	V. sl. pitting on side and bottom seam joint
1-C	8.12	Mod. sed., mod. pitting on side seam	Sl.-mod. pitting on side seam and bottom joint
2-C	8.28	Sl. sed., sl. pitting on side seam	Sl. pitting on side seam and at bottom joint
3-C	8.42	Sl. sed., sl. pitting on side seam, vapor phase corrosion	Sl. pitting on side seam and at bottom joint
4-C	9.00	Sl. sed., sl. pitting on side seam	Sl. pitting on side seam, mod. pitting at bottom joint
5-C	11.18	Soln. clean, v. sl. sed. at bottom joint	Sl. pitting on side seam and at bottom joint

APPENDIX B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ETHYLENE GLYCOL ANTIFREEZE

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Results show that antifreeze compounds with pH values below 10.3 caused corrosion in less than six months. Containers filled with compounds having pH values above 10.3 showed some corrosion in one year and were generally unsatisfactory after two years storage. Most of the attack was at the junction of the bottom and side seams of the containers.

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